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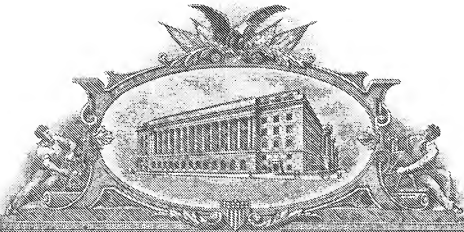
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**STABLE ORGANIC FREE RADICAL POLYMER SYSTEMS:
COMPOSITIONS, PROCESSES, AND ARTICLES OF MANUFACTURE
FIELD OF THE INVENTION**

This invention relates to polymer systems that undergo free radical reactions in the presence of free-radical inducing species, heat, or both.

DESCRIPTION OF THE PRIOR ART

5 A number of polymers can undergo free radical reactions. Some of those reactions are beneficial such as crosslinking or grafting while others are detrimental such as premature crosslinking, competing, or degrading. There is a need to promote the beneficial reactions while minimizing the impact of the detrimental reactions.

10 For example, free-radical crosslinkable polymers undergo free-radical crosslinking when a composition containing free-radical crosslinkable polymers and a peroxide is heated to a temperature that activates the peroxide. To ensure that only the desired reactions occur, the temperature is kept low to avoid premature crosslinking during processing and then the temperature is raised to the desired crosslinking temperature to effect crosslinking at the desired time.

15 Notably, in injection molding, a low injection temperature is required because common organic peroxides decompose over a broad temperature range. For example, practitioners commonly inject crosslinkable polymer compositions containing ethylene/propylene/diene monomer-based polymers and the organic peroxide dicumyl peroxide into a mold at about 100 degrees Celsius (below the peroxide's peak decomposition temperature) and then cure the compositions in the mold with wall temperature set at about 165 degrees Celsius. This large temperature difference (about 65 degrees Celsius) results in a very long crosslinking cycle time, particularly for thick parts, and limits the useful polymers to those having a suitable melting temperature or viscosity profile.

25 Similarly, practitioners extrude crosslinkable polymer compositions at temperatures no higher than 140 degrees Celsius and then pass the resulting fabricated articles through a continuous vulcanization tube at a higher cure temperature to complete crosslinking. Because shear heating from extruder screw speed can induce premature crosslinking, the extrusion output rates are limited.

30 To increase extrusion rates or injection temperatures without premature crosslinking, practitioners add scorch inhibitors or antioxidants to the compositions.

Unfortunately, this approach reduces the cure rate. To overcome the cure rate reduction, practitioners use a longer continuous vulcanization tube when extruding the polymer or sophisticated formulations of the composition for extruded or injection molded polymers.

5 Premature crosslinking and chain scission challenge free-radical functionalization of polyolefins with organic peroxides. Notably, grafting of functional monomers to ethylene polymers is typically limited to polymers having a density of less than about 0.955 grams per cubic centimeter because (1) premature crosslinking at high process temperatures results in an undesirable increase in
10 molecular weight and (2) uniform mixing of the functional monomers is required at low processing temperatures. At the other end of the spectrum, propylene polymers undergo chain scission in the presence of organic peroxides. Reportedly, benzoyl peroxide can mitigate chain scission; however, its use results in an undesirable molecular weight increase.

15 It is desirable to graft functional monomers to olefin polymers without a significant change in molecular weight. It is also desirable to apply grafting technology to ethylene polymers having a density equal to or greater than about 0.955 grams per cubic centimeter. It is further desirable to increase the processing temperature without process-limiting premature crosslinking.

20 In the context of expandable, free-radical crosslinkable compositions, two competing reactions complicate processing the compositions. Processing these compositions is complicated because there are needs to prevent premature scorching, minimize the crosslinking cycle time, and expedite expansion. For example, an expandable, free-radical crosslinkable composition is injection molded to prepare mid
25 soles and outer soles. Typically, the composition contains a free-radical crosslinkable polymer, an organic peroxide, and a chemical blowing agent. Process steps include: (1) injecting the expandable, free-radical crosslinkable composition into a sole mold at about 100 degrees Celsius to avoid premature crosslinking; (2) heating the composition to a temperature suitable for activating the chemical blowing agent and
30 crosslinking the composition; (3) allowing the competing expanding and crosslinking reactions to complete; and (4) opening the mold to allow the sole to expand freely out of the mold.

The post-expansion requirement, along with the coupling of the expansion temperature to the crosslinking temperature, limits the applications into which practitioners can use the expandable, free-radical crosslinkable compositions. For example, the compositions are not useful in manufacturing multicomponent soles, involving multiple colors, polymer densities, and polymeric materials. Similarly, the compositions have limited utility in over-molding applications, including automotive or furniture parts wherein it is desirable to have a foamed article molded over a metal or plastic insert. To extend the use of expandable, free-radical crosslinkable compositions to these applications, it is desirable that practitioners are able to expand and crosslink the compositions in a closed mold and then control post expansion to less than about 1.5%. If practitioners can crosslink the compositions in the mold, there will be no need for functionalizing the polymers to facilitate further crosslinking of the polymer. That is, there will be no need to incorporate functional groups for silane crosslinking into the polymer.

It is desirable to graft a variety of functional groups to provide crosslinking technologies that are alternatives to continuous vulcanization processes. It is further desirable to improve the wetting, adhesion, and paintability of olefin polymers.

SUMMARY OF THE INVENTION

The present invention is a stable organic free radical polymer system. The system is useful as a composition, provides processing advantages over existing crosslinking or grafting technologies, and imparts unique properties to articles of manufacture made therefrom. As a composition, the present invention comprises (a) a free-radical crosslinkable polymer, (b) a free-radical inducing species, and (c) a stable organic free radical, wherein (i) the free-radical crosslinkable polymer and the free-radical inducing species have a nominal crosslinking temperature profile and (ii) the stable organic free radical modifies the crosslinking temperature profile of the combination of the free-radical crosslinkable polymer and the free-radical inducing species such that the temperature for onset of crosslinking is increased while the combination retains its cure rate or achieves a faster cure rate at the nominal cure temperature of the free-radical inducing species. As a process, the system permits the use of high molecular weight free-radical crosslinkable polymers, facilitates higher processing temperatures and rates, protects polymers subject to premature crosslinking or chain scission in free radical environments, decouples competing

temperature dependent reactions from free-radical reactions, and permits alternative grafting technologies. As articles of manufacture, the system permits articles to be made having physical properties previously unachievable in view of limitations posed by previously available processes for preparing free-radical crosslinked polymers.

BRIEF DESCRIPTION OF DRAWING

Fig. 1 shows torque-time curves at 140 degrees Celsius for crosslinkable polymeric compositions with and without a stable organic free radical.

Fig. 2 shows torque-time curves at 180 degrees Celsius for crosslinkable polymeric compositions with and without a stable organic free radical.

Fig. 3 shows torque-time curves at 140 degrees Celsius for the commercially-available SuperOhm™ 3728 peroxide-crosslinkable composition with and without a stable organic free radical.

Fig. 4 shows torque-time curves at 180 degrees Celsius for the commercially-available SuperOhm™ 3728 peroxide-crosslinkable composition with and without a stable organic free radical.

Fig. 5 shows torque-time curves at 150 degrees Celsius for a high density polyethylene (a) as a base polymer, (b) with peroxide, and (c) with peroxide and a stable organic free radical.

Fig. 6 shows spectra from Attenuated Total Reflectance infrared scans of the surface of test specimens prepared from compositions containing a stable organic free radical.

Fig. 7 shows torque-time curves at 165 degrees Celsius for injection-moldable, crosslinkable polymeric compositions with various levels of a stable organic free radical.

Fig. 8 shows torque-time curves at 185 degrees Celsius for injection-moldable, crosslinkable polymeric compositions with various levels of a stable organic free radical.

DESCRIPTION OF THE INVENTION

The invented crosslinkable polymeric composition comprises (a) a free-radical crosslinkable polymer, (b) a free-radical inducing species, and (c) a stable organic free radical, wherein (i) the free-radical crosslinkable polymer and the free-radical inducing species have a nominal crosslinking temperature profile and (ii) the stable organic free radical modifies the crosslinking temperature profile of the combination

of the free-radical crosslinkable polymer and the free-radical inducing species such that the temperature for onset of crosslinking is increased while the combination retains its cure rate or achieves a faster cure rate at the nominal cure temperature of the free-radical inducing species. The present invention is useful in wire-and-cable, footwear, film (e.g. greenhouse, shrink, and elastic), rheology modification, engineering thermoplastic, highly-filled, flame retardant, reactive compounding, thermoplastic elastomer, thermoplastic vulcanizate, automotive, vulcanized rubber replacement, construction, automotive, furniture, foam, wetting, adhesive, paintable substrate, dyeable polyolefin, moisture-cure, nanocomposite, compatibilizing, printing, steel replacement, wax, sizing, calendared sheet, medical, dispersion, coextrusion, cement/plastic reinforcement, food packaging, non-woven, paper-modification, multilayer container, sporting good, oriented structure, and surface treatment applications.

Preferably, the stable organic free radical increases the cure rate of the combination at the nominal cure temperature of the free-radical inducing species. More preferably, the combination also retains its degree of cure or achieves a higher degree of cure at the nominal cure temperature of the organic peroxide.

A variety of polymers is useful in the present invention. Moreover, many polymers that were heretofore unsuitable for free-radical crosslinking are useful in the present invention. Notably, polymers having a high melting temperature are now suitable for free-radical crosslinking. In particular, the present invention is useful with free-radical crosslinking polymers having (a) a melting temperature equal to or greater than about 130 degrees Celsius, (b) a melting temperature about equal to or less than the flash point of the stable organic free radical, or (c) a time-to-torque rise (TS1) as measured at 140 degrees Celsius by a rheometer of less than about 20 minutes in the absence of a stable organic free radical.

Preferably, the free-radical crosslinkable polymer is hydrocarbon-based. Suitable hydrocarbon-based polymers include ethylene/propylene/diene monomers, ethylene/propylene rubbers, ethylene/alpha-olefin copolymers, ethylene homopolymers, propylene homopolymers, ethylene/styrene interpolymers, ethylene/unsaturated ester copolymers, halogenated polyethylenes, propylene copolymers, natural rubber, styrene/butadiene rubber, styrene/ butadiene/ styrene block copolymers, styrene/ ethylene/ butadiene/ styrene copolymers, polybutadiene

rubber, butyl rubber, chloroprene rubber, chlorosulfonated polyethylene rubber, ethylene/diene copolymer, and nitrile rubber, and blends thereof.

More preferably, the hydrocarbon-based polymer is selected from the group consisting of ethylene/ propylene/ diene monomers and blends of ethylene/ propylene/
5 diene monomers with ethylene/alpha-olefin copolymers.

The present invention is particularly beneficial when the free-radical crosslinkable polymer is a propylene polymer because the stable organic free radical can suppress chain scission of the propylene polymer.

With regard to the suitable ethylene polymers, the free-radical crosslinkable
10 polymers generally fall into four main classifications: (1) highly-branched; (2) heterogeneous linear; (3) homogeneously branched linear; and (4) homogeneously branched substantially linear. These polymers can be prepared with Ziegler-Natta catalysts, metallocene or vanadium-based single-site catalysts, or constrained geometry single-site catalysts.

15 Highly branched ethylene polymers include low density polyethylene (LDPE). Those polymers can be prepared with a free-radical initiator at high temperatures and high pressure. Alternatively, they can be prepared with a coordination catalyst at high temperatures and relatively low pressures. These polymers have a density between about 0.910 grams per cubic centimeter and about 0.940 grams per cubic centimeter
20 as measured by ASTM D-792.

Heterogeneous linear ethylene polymers include linear low density polyethylene (LLDPE), ultra-low density polyethylene (ULDPE), very low density polyethylene (VLDPE), and high density polyethylene (HDPE). Linear low density ethylene polymers have a density between about 0.850 grams per cubic centimeter
25 and about 0.940 grams per cubic centimeter and a melt index between about 0.01 to about 100 grams per 10 minutes as measured by ASTM 1238, condition I. Preferably, the melt index is between about 0.1 to about 50 grams per 10 minutes. Also, preferably, the LLDPE is an interpolymer of ethylene and one or more other alpha-olefins having from 3 to 18 carbon atoms, more preferably from 3 to 8 carbon atoms.
30 Preferred comonomers include 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene.

Ultra-low density polyethylene and very low density polyethylene are known interchangeably. These polymers have a density between about 0.870 grams per cubic centimeter and about 0.910 grams per cubic centimeter. High density ethylene

polymers are generally homopolymers with a density between about 0.941 grams per cubic centimeter and about 0.965 grams per cubic centimeter.

Homogeneously branched linear ethylene polymers include homogeneous LLDPE. The uniformly branched/homogeneous polymers are those polymers in which the comonomer is randomly distributed within a given interpolymer molecule and wherein the interpolymer molecules have a similar ethylene/comonomer ratio within that interpolymer.

Homogeneously-branched substantially linear ethylene polymers include (a) homopolymers of C_2 - C_{20} olefins, such as ethylene, propylene, and 4-methyl-1-pentene, (b) interpolymers of ethylene with at least one C_3 - C_{20} alpha-olefin, C_2 - C_{20} acetylenically unsaturated monomer, C_4 - C_{18} diolefin, or combinations of the monomers, and (c) interpolymers of ethylene with at least one of the C_3 - C_{20} alpha-olefins, diolefins, or acetylenically unsaturated monomers in combination with other unsaturated monomers. These polymers generally have a density between about 0.850 grams per cubic centimeter and about 0.970 grams per cubic centimeter. Preferably, the density is between about 0.85 grams per cubic centimeter and about 0.955 grams per cubic centimeter, more preferably, between about 0.850 grams per cubic centimeter and 0.920 grams per cubic centimeter.

Ethylene/styrene interpolymers useful in the present invention include substantially random interpolymers prepared by polymerizing an olefin monomer (i.e., ethylene, propylene, or alpha-olefin monomer) with a vinylidene aromatic monomer, hindered aliphatic vinylidene monomer, or cycloaliphatic vinylidene monomer. Suitable olefin monomers contain from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Preferred such monomers include ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Most preferred are ethylene and a combination of ethylene with propylene or C_{4-8} alpha-olefins. Optionally, the ethylene/styrene interpolymers polymerization components can also include ethylenically unsaturated monomers such as strained ring olefins. Examples of strained ring olefins include norbornene and C_{1-10} alkyl- or C_{6-10} aryl-substituted norbornenes.

Ethylene/unsaturated ester copolymers useful in the present invention can be prepared by conventional high-pressure techniques. The unsaturated esters can be alkyl acrylates, alkyl methacrylates, or vinyl carboxylates. The alkyl groups can have

1 to 8 carbon atoms and preferably have 1 to 4 carbon atoms. The carboxylate groups can have 2 to 8 carbon atoms and preferably have 2 to 5 carbon atoms. The portion of the copolymer attributed to the ester comonomer can be in the range of about 5 to about 50 percent by weight based on the weight of the copolymer, and is preferably in the range of about 15 to about 40 percent by weight. Examples of the acrylates and methacrylates are ethyl acrylate, methyl acrylate, methyl methacrylate, t-butyl acrylate, n-butyl acrylate, n-butyl methacrylate, and 2-ethylhexyl acrylate. Examples of the vinyl carboxylates are vinyl acetate, vinyl propionate, and vinyl butanoate. The melt index of the ethylene/unsaturated ester copolymers can be in the range of about 0.5 to about 50 grams per 10 minutes.

Halogenated ethylene polymers useful in the present invention include fluorinated, chlorinated, and brominated olefin polymers. The base olefin polymer can be a homopolymer or an interpolymers of olefins having from 2 to 18 carbon atoms. Preferably, the olefin polymer will be an interpolymers of ethylene with propylene or an alpha-olefin monomer having 4 to 8 carbon atoms. Preferred alpha-olefin comonomers include 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. Preferably, the halogenated olefin polymer is a chlorinated polyethylene.

Examples of propylene polymers useful in the present invention include propylene homopolymers and copolymers of propylene with ethylene or another unsaturated comonomer. Copolymers also include terpolymers, tetrapolymers, etc. Typically, the polypropylene copolymers comprise units derived from propylene in an amount of at least about 60 weight percent. Preferably, the propylene monomer is at least about 70 weight percent of the copolymer, more preferably at least about 80 weight percent.

Natural rubbers suitable in the present invention include high molecular weight polymers of isoprene. Preferably, the natural rubber will have a number average degree of polymerization of about 5000 and a broad molecular weight distribution.

Useful styrene/butadiene rubbers include random copolymers of styrene and butadiene. Typically, these rubbers are produced by free radical polymerization. Styrene/butadiene/styrene block copolymers of the present invention are a phase-separated system. The styrene/ethylene/butadiene/styrene copolymers useful in the

present invention are prepared from the hydrogenation of styrene/butadiene/styrene copolymers.

The polybutadiene rubber useful in the present invention is preferably a homopolymer of 1,4-butadiene. Preferably, the butyl rubber of the present invention
5 is a copolymer of isobutylene and isoprene. The isoprene is typically used in an amount between about 1.0 weight percent and about 3.0 weight percent.

For the present invention, polychloroprene rubbers are generally polymers of 2-chloro-1,3-butadiene. Preferably, the rubber is produced by an emulsion polymerization. Additionally, the polymerization can occur in the presence of sulfur
10 to incorporate crosslinking in the polymer.

Preferably, the nitrile rubber of the present invention is a random copolymer of butadiene and acrylonitrile.

Other useful free-radical crosslinkable polymers include silicone rubbers and fluorocarbon rubbers. Silicone rubbers include rubbers with a siloxane backbone of
15 the form -Si-O-Si-O- . Fluorocarbon rubbers useful in the present invention include copolymers or terpolymers of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene with a cure site monomer to permit free-radical crosslinking.

Useful free-radical inducing species include organic peroxides, Azo free radical initiators, and bicumene. Preferably, the free-radical inducing species is an
20 organic peroxide. Also, oxygen-rich environments can initiate useful free-radicals. Preferable organic peroxides include dicumyl peroxide and Vulcup R. The organic peroxide can be added via direct injection. Preferably, the free-radical inducing species is present in an amount between about 0.5 weight percent and about 5.0 weight percent, more preferably, between about 0.5 weight percent and about 2.0
25 weight percent.

The stable organic free radicals useful in the present invention include (i) hindered amine-derived stable organic free radicals, (ii) iniferters, (iii) organometallic compounds, and (iv) aryl azoxy radical. Preferably, the stable organic free radical is a hindered amine-derived stable organic free radical selected from the group
30 consisting of 2,2,6,6-tetramethyl piperidinyl oxy (TEMPO) and its derivatives. More preferably, the stable organic free radical is bis-TEMPO, oxo-TEMPO, hydroxy-TEMPO, an ester of hydroxy-TEMPO, polymer-bound TEMPO, PROXYL, DOXYL, di-tertiary butyl N oxyl, dimethyl diphenylpyrrolidine-1-oxyl, 4 phosphonoxo

TEMPO, or a metal complex with TEMPO. Even more preferably, the stable organic free radical is bis-TEMPO or hydroxy-TEMPO.

Iniferters are compounds capable of initiating and terminating free radical reactions. They are also capable of reversibly terminating growing polymer chains.

- 5 When the stable organic free radical is an iniferter, it is preferably selected from the group consisting of tetraethyl thiuram disulfide, benzyl NN diethyldithiocarbamate, dithiocarbamate, polythiocarbamate, and S benzyl dithiocarbamate.

When the stable organic free radical is a component is a crosslinkable polymeric composition, the stable organic free radical of the present invention permits

- 10 (a) processing the free-radical crosslinkable polymer at a temperature higher than achievable in the absence of the stable organic free radical and (b) maintaining the time-to-torque rise (TS1) as measured by a rheometer at that temperature at greater than about 20 minutes. The stable organic free radical also permits (a) processing the free-radical crosslinkable polymer at a rate faster than achievable in the absence of the
- 15 stable organic free radical and (b) maintaining the time-to-torque rise (TS1) as measured by a rheometer at that temperature at greater than about 20 minutes.

When the stable organic free radical is a component is a crosslinkable polymeric composition, the stable organic free radical is present in an amount less than about 2 weight percent, more preferably, less than about 1 weight percent. Even

20 more preferably, the stable organic free radical is present in an amount less than about 0.5 weight percent, most preferably, less than 0.25 weight percent. Preferably, the free-radical inducing species and the stable organic free radical are present in a ratio greater than about 1, more preferably, between about 1 to about 20. Preferably, the stable organic free radical is uniformly distributed in the crosslinkable polymeric

25 composition.

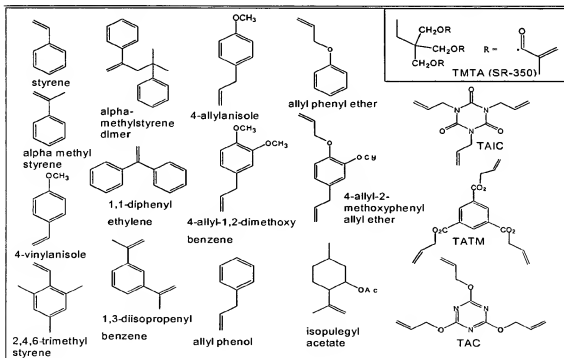
The crosslinkable polymeric composition can also contain an organic crosslinking modifier not having a double bond, wherein the organic crosslinking modifier and the stable organic free radical synergistically (a) suppress the crosslinking rate of the free-radical crosslinkable polymer at temperatures less than

30 the nominal cure temperature of the free-radical inducing species and (b) enhance the crosslinking density at the nominal cure temperature of the free-radical inducing species. Preferably, the organic crosslinking modifier is tris(2,4-di-tert-butylphenyl)phosphite, poly[[6-[(1,1,3,3,-tetramethyl-butyl)amino]-s-triazine-2,4-

diyl][2,2,6,6-tetramethyl-4-piperidyl]imino]hexamethylene[2,2,6,6-tetramethyl-4-piperidyl]imino)], 2(2'-hydroxy-3',5'-di-tert-amylphenyl)benzotriazole, or blends thereof.

5 The crosslinkable polymeric composition can also contain a nonpolar additive, wherein the additive enhances the crosslinking performance without contributing to the migration of the stable organic free radical to the surface of an article of manufacture prepared from the crosslinkable polymeric composition. Preferably, the nonpolar additive is decadiene or polybutadiene.

10 The crosslinkable polymeric composition can also contain a cure booster or a coagent to enhance the crosslinking performance of the free-radical inducing species, without increasing the free-radical inducing species. Crosslinking performance enhancements can include cure rate and cure degree. The addition of a cure booster is particularly useful when the free-radical crosslinkable polymer is a chlorinated polyethylene. Useful cure boosters include polyvinyl agents and certain monovinyl
15 agents such as alpha methyl styrene dimer, allyl pentaerythritol (or pentaerythritol triacrylate), TAC, TAIC, 4-allyl-2-methoxyphenyl allyl ether, and 1,3-diisopropenylbenzene. Other useful cure boosters include compounds having the following chemical structures.



The crosslinkable polymeric composition can also contain a chemical or physical blowing agent, thereby rendering the crosslinkable polymeric composition expandable. Preferably, the blowing agent will be a chemical blowing agent. An example of a useful chemical blowing agent is azodicarbonamide.

5 Other additives are useful with the crosslinkable polymeric composition of the present invention. Those additives include scorch inhibitors, antioxidants, fillers, clays, processing aids, carbon black, flame retardants, peroxides, other polymers, and colorants. The crosslinkable polymeric compositions can be highly filled or semiconductive.

10 In a preferred embodiment, the present invention is an article of manufacture prepared from the crosslinkable polymeric composition. The benefits of the present inventions are particularly apparent with thick articles of manufacture. Any number of processes can be used to prepare the articles of manufacture. Specifically useful processes include injection molding, extrusion, compression molding, rotational
15 molding, thermoforming, blowmolding, powder coating, Banbury batch mixers, fiber spinning, and calendaring. Suitable articles of manufacture include wire-and-cable insulations, wire-and-cable semiconductive articles, wire-and-cable coatings and jackets, cable accessories, shoe soles, multicomponent shoe soles (including polymers of different densities and type), weather stripping, gaskets, profiles, durable goods,
20 rigid ultradrawn tape, run flat tire inserts, construction panels, composites (e.g., wood composites), pipes, foams, and fibers (including binder fibers and elastic fibers).

The stable organic free radical and free-radical inducing species can be combined with the free-radical crosslinkable polymer in a variety of ways, including direct compounding, direct soaking, and direct injection.

25 In another embodiment of the present invention, the invention is a process for preparing an article of manufacture comprising the steps of (a) injecting at an injection temperature the crosslinkable polymeric composition into a mold at a mold temperature; and (b) heating the crosslinkable polymeric composition in the mold for a period of time to a crosslinking temperature sufficient to crosslink the crosslinkable
30 polymeric composition. Preferably, the process will have T_0 being the maximum injection temperature achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at that injection

temperature, T_1 being the nominal crosslinking temperature of the free-radical crosslinkable polymeric composition, ΔT being the difference between T_1 and T_0 , and the stable organic free radical permitting a reduction in (i) ΔT by 20% and (ii) the time required to heat the crosslinkable polymeric composition to the crosslinking temperature.

Also, preferably, the process will have (1) MPR being the maximum processing rate achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at the injection temperature and (2) the stable organic free radical permitting (a) an increase in MPR by 20% and (b) maintenance of TS1 at greater than about 20 minutes.

In another alternate embodiment, the present invention is a process for preparing an article of manufacture comprising the steps of (a) extruding the crosslinkable polymeric composition at an extrusion temperature; and (b) heating the crosslinkable polymeric composition for a period of time to a crosslinking temperature sufficient to crosslink the crosslinkable polymeric composition. Preferably, the stable organic free radical in the process permits extruding the free-radical crosslinkable polymer at a throughput rate higher than achievable in the absence of the stable organic free radical. More preferably, the throughput rate is at least about 20% faster than achievable in the absence of the stable organic free radical. Preferably, the process will have T_0 being the maximum extrusion temperature achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at that extrusion temperature, T_1 being the nominal crosslinking temperature of the free-radical crosslinkable polymeric composition, ΔT being the difference between T_1 and T_0 , and the stable organic free radical permitting a reduction in (i) ΔT by 20% and (ii) the time required to heat the crosslinkable polymeric composition to the crosslinking temperature.

Also, preferably, the process will (1) MPR being the maximum processing rate achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at the extrusion temperature and (2) the

stable organic free radical permits (a) increasing MPR by 20% and (b) maintaining TS1 at greater than about 20 minutes.

In an alternate embodiment of the present invention, the invention is a process for preparing an article of manufacture comprising the steps of (a) injecting at an injection temperature an expandable, crosslinkable polymeric composition into a mold at a mold temperature; (b) heating the expandable, crosslinkable polymeric composition for a period of time to a crosslinking temperature sufficient to expand and crosslink the expandable, crosslinkable polymeric composition; (c) removing the expandable, crosslinkable polymeric composition from the mold; and (d) expanding and crosslinking the expandable, crosslinkable polymeric composition to an expanded, crosslinked article of manufacture. Preferably, the process will have T_0 being the maximum injection temperature achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at that injection temperature, T_1 being the nominal crosslinking temperature of the free-radical crosslinkable polymeric composition, ΔT being the difference between T_1 and T_0 , and the stable organic free radical permitting a reduction in (i) ΔT by 20% and (ii) the time required to heat the expandable, crosslinkable polymeric composition to the crosslinking temperature.

Also, preferably, the process will have (1) MPR being the maximum processing rate achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at the injection temperature and (2) the stable organic free radical permitting (a) an increase in MPR by 20% and (b) maintenance of TS1 at greater than about 20 minutes.

In another embodiment of the present invention, the invention is a time/temperature stable masterbatch for preparing a crosslinkable polymeric composition comprising (a) a carrier polymer and (b) a stable organic free radical present in an amount less than about 15 weight percent, wherein (1) the masterbatch having suitable time and temperature stability for shelf storage and to permit delayed mixing of the masterbatch with a free-radical crosslinkable polymer and a free-radical inducing species, (2) the crosslinkable polymeric composition comprises (i) the free-radical crosslinkable polymer, (ii) the free-radical inducing species, and (iii) the stable

organic free radical, (3) the free-radical crosslinkable polymer and the free-radical inducing species have a nominal crosslinking temperature profile, and (4) the stable organic free radical modifies the crosslinking temperature profile of the combination of the free-radical crosslinkable polymer and the free-radical inducing species such that the temperature for onset of crosslinking is increased while the combination retains its cure rate or achieves a faster cure rate at the nominal cure temperature of the free-radical inducing species. Preferably, the carrier polymer in the process will be a free-radical crosslinkable polymer.

The time/temperature stable masterbatch can also contain a stabilizer, being capable to disperse the stable organic free radical in the masterbatch. Preferably, the stabilizer will have a melting temperature equal to or greater than about 90 degrees Celsius. More preferably, the stabilizer will be zinc stearate.

In yet another embodiment, the present invention is an expandable, crosslinkable polymeric composition comprising (a) a free-radical crosslinkable polymer; (b) a free-radical inducing species; (c) a stable organic free radical; and (d) a blowing agent selected from the group consisting of chemical blowing agents and physical blowing agents, wherein (i) the free-radical crosslinkable polymer and the free-radical inducing species have a nominal crosslinking temperature profile, (ii) the activation temperature of the chemical blowing agent falls within the nominal crosslinking temperature profile, (iii) the stable organic free radical modifies the crosslinking temperature profile of the combination of the free-radical crosslinkable polymer and the free-radical inducing species such that (1) the temperature for onset of crosslinking is increased while the combination retains its cure rate at the nominal cure temperature of the free-radical inducing species and (2) the activation of the blowing agent is decoupled from the modified crosslinking temperature profile of the free-radical crosslinkable polymer and the free-radical inducing species. This embodiment includes articles of manufacture prepared from the expandable, crosslinkable polymeric composition and the processes for preparing the articles of manufacture.

Specifically, the present embodiment includes the process comprising the steps of (a) injecting at an injection temperature the expandable, crosslinkable polymeric composition into a mold at a mold temperature; (b) heating the expandable, crosslinkable polymeric composition in the mold for a period of time to the activation

temperature of the blowing agent; (c) expanding the expandable, crosslinkable polymeric composition to an expanded, crosslinkable polymeric composition in the mold; and. (d) crosslinking the expanded, crosslinkable polymeric composition to an expanded, crosslinked polymeric composition in the mold. Preferably, the expandable, crosslinkable polymeric composition will have crosslinking at the end of Step (b) to provide sufficient melt strength to support a stable foam structure.

Also, preferably, the process will have T_0 being the maximum injection temperature achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at that injection temperature, T_1 being the nominal crosslinking temperature of the free-radical crosslinkable polymeric composition, ΔT being the difference between T_1 and T_0 , and the stable organic free radical permitting a reduction in (i) ΔT by 20% and (ii) the time required to heat the expandable, crosslinkable polymeric composition to the crosslinking temperature.

Also, preferably, the process will have (1) MPR being the maximum processing rate achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at the injection temperature and (2) the stable organic free radical permitting (a) an increase in MPR by 20% and (b) maintenance of TS1 at greater than about 20 minutes.

Also, the present embodiment specifically includes the process comprising the steps of (a) injecting at an injection temperature the expandable, crosslinkable polymeric composition into a mold at a mold temperature; (b) heating the expandable, crosslinkable polymeric composition in the mold for a period of time to the activation temperature of the blowing agent; (c) expanding the expandable, crosslinkable polymeric composition to an expanded, crosslinkable polymeric composition in the mold; (d) heating the expanded, crosslinkable polymeric composition for a period of time to a crosslinking temperature sufficient to crosslink the expanded, crosslinkable polymeric composition; and (e) crosslinking the expanded, crosslinkable polymeric composition to an expanded, crosslinked polymeric composition in the mold. Preferably, the expandable, crosslinkable polymeric composition will have

crosslinking at the end of Step (b) to provide sufficient melt strength to support a stable foam structure.

Also, preferably, the process will have T_0 being the maximum injection temperature achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at that injection temperature, T_1 being the nominal crosslinking temperature of the free-radical crosslinkable polymeric composition, ΔT being the difference between T_1 and T_0 , and the stable organic free radical permitting reduction of (i) ΔT by 20% and (ii) the time required to heat the crosslinkable polymeric composition to the activation temperature.

Also, preferably, the process will have (1) MPR being the maximum processing rate achievable for the free-radical crosslinkable polymer in the absence of the stable organic free radical while maintaining the time-to-torque rise (TS1) at no less than about 20 minutes as measured by a rheometer at the injection temperature and (2) the stable organic free radical permitting (a) an increase in MPR by 20% and (b) maintenance of TS1 at greater than about 20 minutes.

In yet another embodiment, the present invention is a process for preparing a functionalized polymer comprising the steps of (a) preparing a polymer-matrix mixture by admixing and heating (i) a polymer being capable of forming free radicals when induced by a free-radical inducing species, (ii) a free-radical inducing species, (iii) a stable organic free radical, and (iv) a graftable monomer and (b) grafting the graftable monomer onto the polymer to form a functionalized polymer, wherein the stable organic free radical substantially prevents crosslinking of the polymer during Step (a), thereby preferentially promoting the grafting of the graftable monomer onto the polymer in Step (b). Preferably, the mixing step renders the free-radical inducing species and the graftable monomer uniformly distributed in the polymer-matrix mixture.

The process may be continuous or batch. As a continuous process, the process will preferably have a residence time in an extruder of less than about 60 seconds. More preferably, the residence time will be less than about 35 seconds.

Also, preferably, the process yields a functionalized polymer having certain properties substantially similar to nonfunctionalized base polymer. Those desired

properties include gel content, melt index, and melt index ratio (I10/I2). Preferably, the resulting functionalized polymer with a melt index ratio reduction of less than about 30, more preferably, less about 20, and even more preferably, less than about 15. Most preferably, the melt index ratio reduction is less than about 10.

5 Examples of polymers being capable of forming free radicals include the previously-identified free-radical crosslinkable polymers. Preferably, the polymers are olefin-based. More preferably, the polymers include polymers, which in the absence of the stable organic free radical and while in the presence of a free-radical inducing species, are susceptible to a reduction of melt index ratio (I10/I2) of greater
10 than about 20 when processed at a temperature suitable for grafting the graftable monomer onto the polymer.

 Examples of useful graftable monomers are maleic anhydride and silanes. The resulting grafting level is preferably greater than about 0.5 weight percent monomer. More preferably, the grafting level is greater than about 1.0 weight percent monomer.
15 Most preferably, the grafting level is greater than about 1.5 weight percent monomer.

 In yet another embodiment, the present invention is a process for preparing a functionalized polymer comprising the steps of (a) preparing a polymer-matrix mixture by admixing and heating (i) a polymer being capable of forming free radicals when induced by a free-radical inducing species, (ii) a free-radical inducing species,
20 (iii) a stable organic free radical, and (iv) a graftable monomer and (b) grafting the graftable monomer onto the polymer to form a functionalized polymer, wherein the stable organic free radical substantially prevents chain scission of the polymer during Step (a), thereby preferentially promoting the grafting of the graftable monomer onto the polymer in Step (b). Preferably, the free-radical inducing species is present in
25 amount between about 0.02 weight percent and about 0.08 weight percent, the stable organic free radical is present in amount between about 0.03 weight percent and about 0.10 weight percent, and the graftable monomer is present in amount between about 0.10 weight percent and about 5.0 weight percent. This invention also includes articles of manufacture made from the functionalized polymer.

30 In yet another embodiment, the present invention is a process for preparing a functionalized polymer comprising the steps of (a) forming a polymer-matrix mixture by mixing and heating (i) a base polymer being capable of forming free radicals in the presence of a free-radical inducing species, (ii) a free-radical-inducing species, and

(iii) a stable organic free radical, and (b) grafting the stable organic free radical onto the base polymer to form a functionalized polymer. This embodiment includes articles of manufacture made from the functionalized polymer and processes that use the resulting functionalized polymer. Preferably, the polymer will be substantially
5 free of chain scission during the process.

Also, preferably, the stable organic free radical will have hydroxy functionality. More preferably, the stable organic free radical will be hydroxy-TEMPO.

Also, preferably, the resulting functionalized polymer will be a hydroxy-
10 functionalized polymer. More preferably, the functionalized polymer will be a branched polymer. Even more preferably, the branched polymer will have a melt index ratio (I10/I2) greater than the base polymer. Also, even more preferably, the branched polymer will have a notched-IZOD impact strength or melt strength greater than the base polymer. This invention also or the branched polymer.

15 Preferably, the present invention is also process for preparing a urethane-crosslinked polymer comprising the steps of (a) heating the hydroxy-functionalized polymer; (b) admixing an isocyanate; and (c) forming urethane linkages to crosslink the hydroxy-functionalized polymer. More preferably, the urethane linkages are formed by cooling the mixture. Also, preferably, the rheology of the functionalized
20 polymer is substantially similar to the rheology of the polymer before being functionalized by the functionalizing process.

In another embodiment, the present invention is a reaction product prepared by reacting a hydroxy-functionalized stable organic free radical with an isocyanate, processes using the reaction product, hydroxy-functionalized polymers prepared by
25 those processes, and related articles of manufacture. Preferably, the hydroxy-functionalized stable organic free radical is hydroxy-TEMPO. Also, preferably, the isocyanate is a diisocyanate or a polymeric diisocyanate.

A preferred process included in the present embodiment prepares a hydroxy-functionalized polymer using the steps of (a) forming a polymer-matrix mixture by
30 mixing (i) a polymer being capable of forming free radicals when induced by a free-radical inducing species, (ii) a free-radical inducing species, and (iii) the reaction product; (b) heating the polymer-matrix mixture; and (c) grafting the reaction product onto the polymer to form a hydroxy-functionalized polymer. More preferably, the

process also has the step of (d) forming urethane linkages to crosslink the hydroxy-functionalized polymer. Even more preferably, the urethane linkages are formed by cooling the mixture.

EXAMPLES

5 The following non-limiting examples illustrate the invention.

A Stable Organic Free Radical Exemplified

Comparative Example 1 and Example 2 were prepared with Affinity™ 8200 polyethylene, having a melt index of 5.0 grams per cubic centimeter and a density of 0.87 grams per cubic centimeter. Affinity™ 8200 polyethylene is available from The
10 Dow Chemical Company. Dicumyl peroxide (DiCup R) was added to each exemplified composition in about 1.00 weight percent. The stable organic free radical, 4-hydroxy-TEMPO was added to the Example 2 composition in about 0.20 weight percent. The remainder of each composition was the polyethylene resin.

Property	Comparative Example 1	Example 2
ML (pound-inches) @ 140 degrees Celsius	0.16	0.16
TS 0.01 (minutes) @ 140 degrees Celsius	1	7.5
ML (pound-inches) @ 180 degrees Celsius	0.84	1.09
MH (pound-inches) @ 180 degrees Celsius	2.98	2.83
t90	4.07	3.94

15 TS 0.01 – the time required to have a torque increase of 0.01 pounds-inch from the minimum torque

t90 – the time required to reach 90% of the ultimate cure level

The TS 0.01 results show that the crosslinkable polymeric composition (containing a stable organic free radical) has a significantly longer scorch inhibition
20 time than its comparative composition without the stable organic free radical. The t90 results indicate a similar cure rate between the crosslinkable polymeric composition and its comparative composition. See Figures 1 and 2.

Impact of a Stable Organic Free Radical in a Commercial Composition

Comparative Example 3 and Example 4 were prepared with SuperOhm™ 3728 peroxide-crosslinkable composition, which is a filled ethylene/propylene/diene monomer composition published and available from Schulman. The composition exemplifying the present invention contained about 0.25 weight percent of the stable organic free radical, 4-hydroxy-TEMPO. The remainder of each composition was the SuperOhm™ 3728 formulation.

Property	Comparative Example 3	Example 4
ML (pound-inches) @ 140 degrees Celsius	1.13	1.03
TS 0.01 (minutes) @ 140 degrees Celsius	<1	17
TS 1 (minutes) @ 140 degrees Celsius	14.4	>30
ML (pound-inches) @ 180 degrees Celsius	0.76	0.78
MH (pound-inches) @ 180 degrees Celsius	10.68	8.01
t90	4.05	4.00

TS 1 – the time required to have a torque increase of 1 pounds-inch from the minimum torque

The TS 0.01 and TS 1 results show that the crosslinkable polymeric composition (containing a stable organic free radical) has a significantly longer scorch inhibition time than its comparative composition without the stable organic free radical. The t90 results indicate a similar cure rate between the crosslinkable polymeric composition and its comparative composition. See Figures 3 and 4.

Impact of a Stable Organic Free Radical on a High Density Polyethylene

Comparative Examples 5 and 6 and Example 7 were prepared with DGDL-3364 high density polyethylene. Dicumyl peroxide (DiCup R) was added to Comparative Example 5 and Example 7 in about 1.00 weight percent. The stable

organic free radical, 4-hydroxy-TEMPO was added to the Example 7 composition in about 0.20 weight percent. The remainder of Comparative Example 5 and Example 7 was the high density polyethylene. Comparative Example 6 was only the high density polyethylene resin, without the stable organic free radical or peroxide added.

- 5 Figure 5 shows the impact of the stable organic free radical on the onset of crosslinking at 150 degrees Celsius.

Comparative Examples 8-15 and Examples 16-27

- 10 A Brabender mixer was used to make 40 gram samples of the blends by adding all ingredients except Dicap R at 125°C for 3 minutes (except CE7 and Ex. 10 in which case the temperature was set at 135°C due to the relatively high viscosity and melting point of the resin). Next, the Dicap R was added and compounded for another 4 minutes. The crosslinking kinetics of the blends was investigated using MDR at 140°C (to simulate extrusion conditions where premature crosslinking is not
15 desirable) and at 182°C (to simulate vulcanization conditions in which rapid and effective crosslinking is desirable).

The following resins were used to prepare the exemplified compositions. Each of the resins is available from The Dow Chemical Company.

Resin	Melt Index, I2 (dg/min)	I21/I2	Density (g/cc)	Melting Point, Tm (°C)
Mirathen CY 7423 LDPE	2.1	53	0.9184	110.0
DXM-446 LDPE	2.4	52	0.9200	110.2
LDPE 5101	1.9	43	0.9183	109.3
Attane 4404G LLDPE	4.4	30	0.9050	118.7
Dowlex 2247G LLDPE	2.3	26	0.9172	120.7
Dowlex 3010 LLDPE	5.3	28	0.9236	122.4
DGDA-2490 NT 3408 HDPE	0.07	83	0.9497	131.2

Comparative Example 28 and Examples 29-33

Each of Comparative Example 28 and Examples 29-33 used a standard peroxide-crosslinkable base composition. To each exemplified composition (i.e., Examples 29-33), 0.28 weight percent of a stable organic free radical, 4-hydroxy-TEMPO was added.

Component / Properties	C.E. 28	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33
Base composition		99.72	99.44	99.44	99.44	99.44
4-hydroxy-TEMPO		0.28	0.28	0.28	0.28	0.28
allyl pentaerythritol			0.28			
2,4-diphenyl-4-methyl-1-pentene				0.28		
Sartomer SR 350					0.28	
Sartomer SR 507						0.28
Total		100	100	100	100	100
@177 degrees Celsius for 12 minutes						
ML (lb-in)	2.34	2.27	2.26	2.23	2.24	2.26
MH (lb-in)	15.81	14.39	14.3	13.68	15.42	14.44
TS1 (min)	0.44	0.76	0.77	0.84	0.79	0.8
TS2 (min)	0.62	0.97	0.98	1.06	1.01	1.02
t10 (min)	0.48	0.79	0.8	0.87	0.83	0.83
t50 (min)	1.16	1.51	1.51	1.55	1.73	1.55
t90 (min)	3.11	3.61	3.55	3.58	4.17	3.65
Cure rate index: 100/(t90-TS2)	40.2	37.9	38.9	39.7	31.6	38.0
Onset cure time at 140 degrees Celsius (min)	3	15.5	15.5	15.5	15.5	15.5

Examples 34-36 (Effect of High Melting Stabilizer)

Each of Examples 34-36 used Nordel IP 3722. To each exemplified composition, 6.0 weight percent of a stable organic free radical, 4-hydroxy-TEMPO was added. The compositions also contained 1.00 weight percent of DFDB-5410 BK.

Component	Example 34	Example 35	Example 36
Nordel IP 3722	93.00	89.00	87.00
4-hydroxy TEMPO	6.00	6.00	6.00
Sartomer SR 350			2.00
Zinc Stearate		4.00	4.00
DFDB-5410 BK	1.00	1.00	1.00
TOTAL	100.00	100.00	100.00

The surfaces of the samples were analyzed by Attenuated Total Reflectance (ATR) infrared. The spectra were collected at several different areas of the same sample. The results showed that the least amount of h-TEMPO was detected on surface of Example 35 while the highest amount was found on Example 36. See Figure 6, which is a plot of ATR results.

Examples 37-41 – Ethylene/Vinyl acetate Copolymer Formulations

Each of Examples 37-41 used Elvax 460 ethylene/vinyl acetate copolymer in standard injection molding formulations.

Component	Exam. 37	Exam. 38	Exam. 39	Exam. 40	Exam. 41
EVA (Elvax 460)	100	100	100	100	100
Perkadox 1440	3	3	3	3	3
CaCO ₃ Omyalite 95T	5	5	5	5	5
ZnSt	0.1	0.1	0.1	0.1	0.1
Irganox B225	0.1	0.1	0.1	0.1	0.1
Hydroxy TEMPO	0.1	0.2	0.3	0.4	0.5

See Figures 7 and 8 show torque-time curves at 165 degrees Celsius and 185 degrees Celsius respectively for the exemplified compositions.

ABSTRACT

The present invention is a stable organic free radical polymer system. The system is useful as a composition, provides processing advantages over existing crosslinking or grafting technologies, and imparts unique properties to articles of manufacture made therefrom. As a composition, the present invention comprises (a) a free-radical crosslinkable polymer, (b) a free-radical inducing species, and (c) a stable organic free radical, wherein (i) the free-radical crosslinkable polymer and the free-radical inducing species have a nominal crosslinking temperature profile and (ii) the stable organic free radical modifies the crosslinking temperature profile of the combination of the free-radical crosslinkable polymer and the free-radical inducing species such that the temperature for onset of crosslinking is increased while the combination retains its cure rate or achieves a faster cure rate at the nominal cure temperature of the free-radical inducing species. As a process, the system permits the use of high molecular weight free-radical crosslinkable polymers, facilitates higher processing temperatures and rates, protects polymers subject to premature crosslinking or chain scission in free radical environments, decouples competing temperature dependent reactions from free-radical reactions, and permits alternative grafting technologies. As articles of manufacture, the system permits articles to be made having physical properties previously unachievable in view of limitations posed by previously available processes for preparing free-radical crosslinked polymers.

Fig. 1

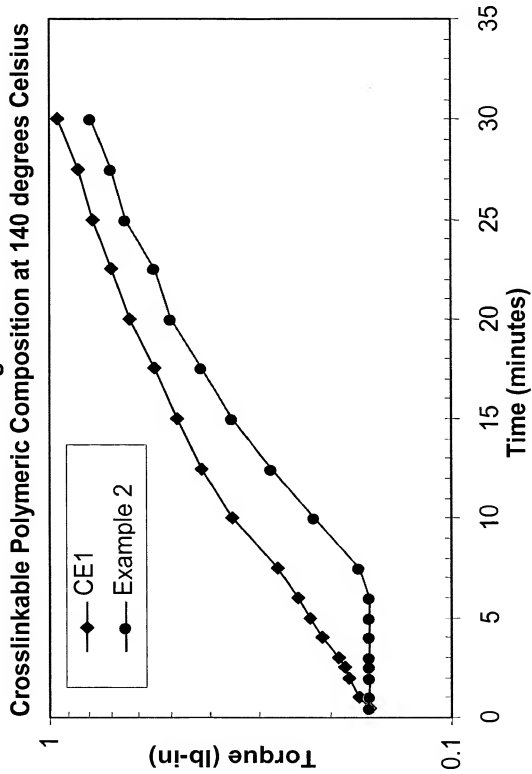


Fig. 2

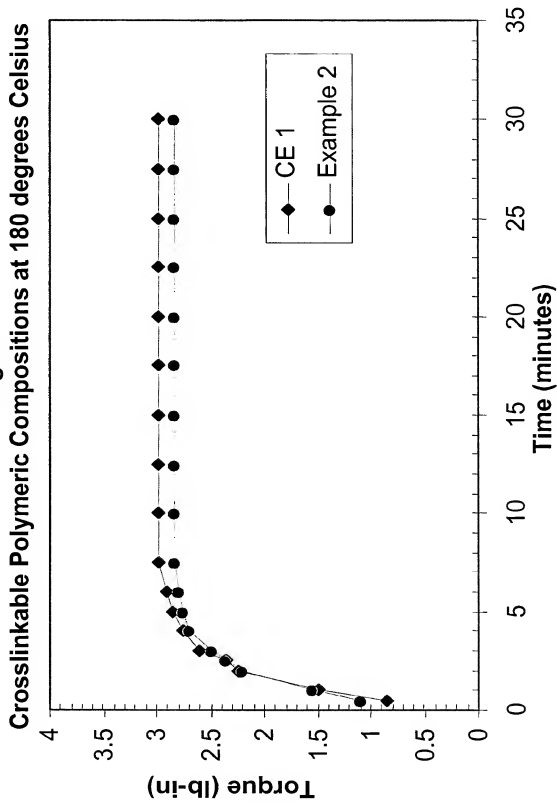


Fig. 3
SuperOhm 3728 Compositions at 140 degrees Celsius

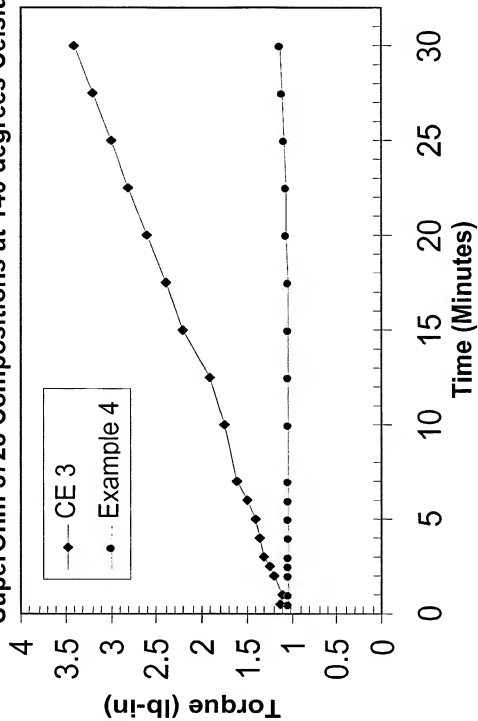


Fig. 4
SuperOhm 3728 Compositions at 180 degrees Celsius

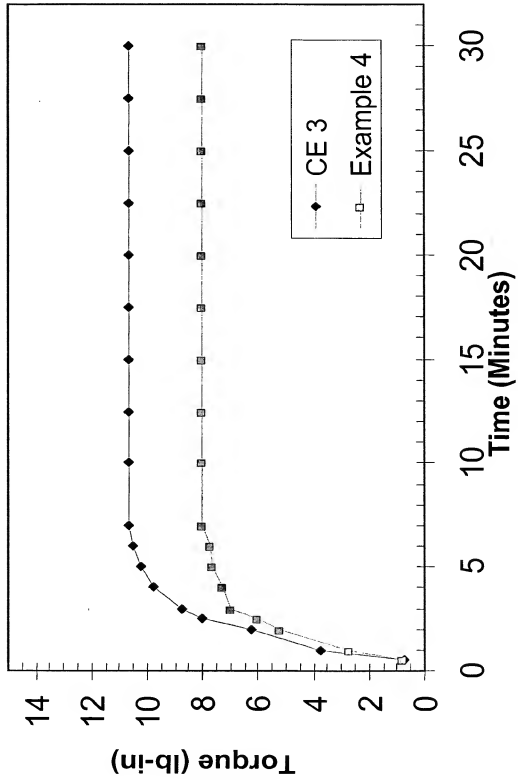


Fig. 5 - High Density Polyethylene Compositions at 150 degrees Celsius

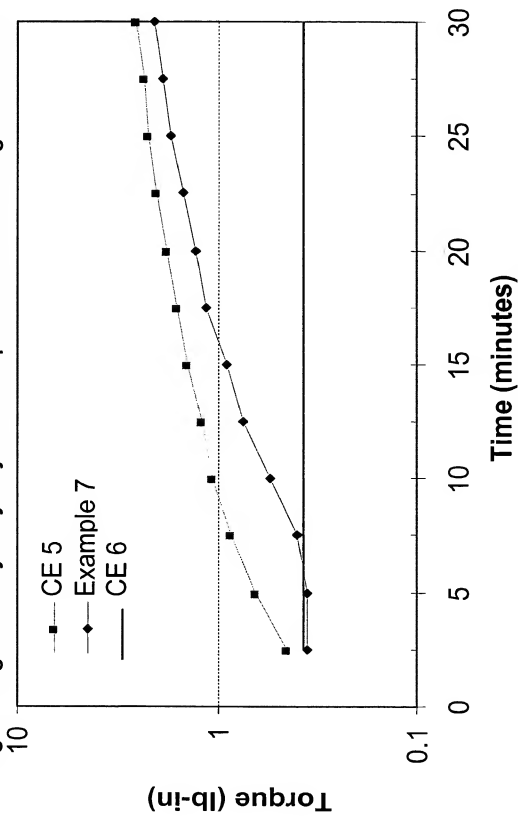


Fig. 6 Attenuated Total Reflectance

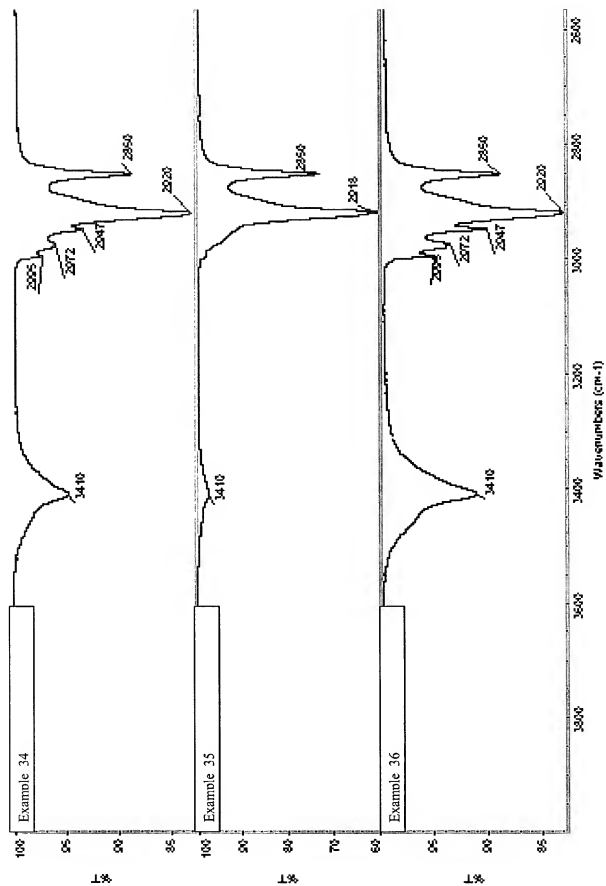


Fig. 7 MDR at 165 Degrees C

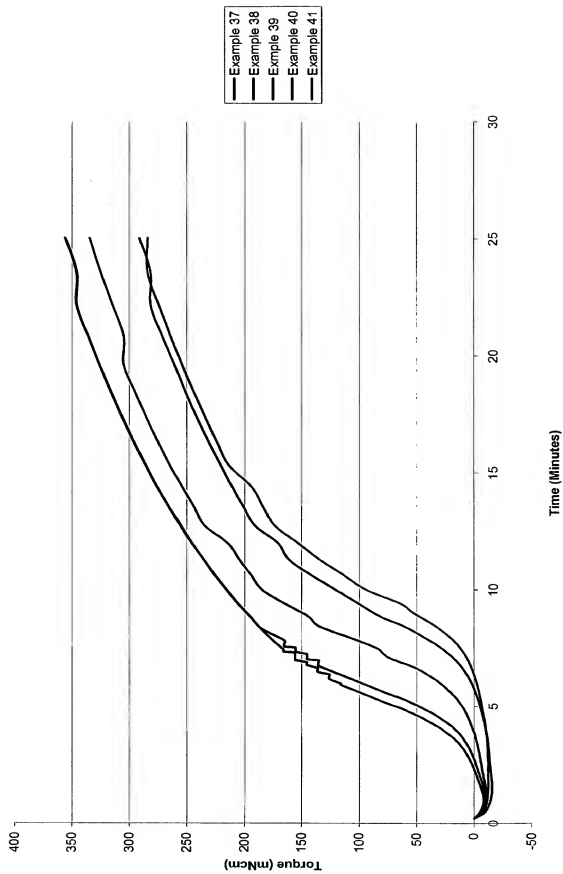


Fig. 8 - MDR at 185 degrees C

